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STUDIES OF GRAPHITE VAPORIZATION USING A
MODULATED BEAM MASS SPECTROMETER

Warren C. Steele, et al

Avco Systems Division

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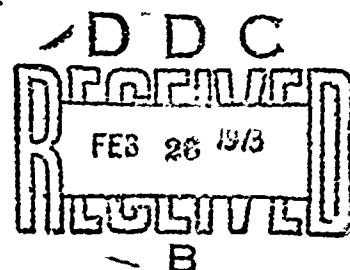
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<p>A set of experiments employing a mass spectrometer to study the kinetics and thermodynamics of graphite vaporization are described. Evidence for the existence of small amounts of C_{10}, C_{11}, C_{14}, and C_{15} in the vapors over hot graphite at about $3000^{\circ}K$ is presented and discussed. Reflection of C_3 vapor by graphite surfaces has been shown to occur without condensation or exchange interaction for surface temperatures in the range $1000^{\circ}K < T_s < 2700^{\circ}K$. Isotopic labelling has been employed to demonstrate significant exchange between C_3 molecules condensed on the surface and atoms from the graphite substrate. A mass spectrum for C_3 is presented.</p>			

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FOREWORD

This report was prepared by Avco Systems Division, Lowell, Massachusetts 01851, under USAF Contract F33615-71-C-1509. This contract was initiated under Project No. 7360, "Thermal and Chemical Behavior of Advanced Weapon System Materials," Task No. 736001, "Chemical, Physical, and Thermodynamic Properties of Aircraft, Missile and Spacecraft Materials." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, LPH, with Paul W. Dimiduk acting as Project Engineer.

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The work at Avco Systems Division was performed by Dr. Warren C. Steele and Mr. Frederick N. Bourgelas. Dr. Steele served as Project Leader. The guidance of Mr. Paul W. Dimiduk of the Air Force Materials Laboratory is gratefully acknowledged.

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This report has been reviewed and is approved.

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I. INTRODUCTION

Graphite and other graphitic materials, such as carbon-carbon composites, possess many desirable high temperature characteristics, making these materials prime candidates for advanced re-entry vehicle applications, particularly where severe re-entry trajectories require survival under extreme conditions. There is now substantial evidence¹ that the ablative response of graphite involves material removal by vaporization, by heterogeneous chemical reaction (oxidation), and by solid particle erosion. Mathematical modeling of the ablation process, which will allow designers of graphitic components to calculate recession rates, etc., depends, in part, on a detailed understanding of the vaporization kinetics and thermochemistry of graphite. It is the purpose of this program to elucidate certain fundamental aspects of the graphite vaporization processes.

In answer to an earlier need for a new and advanced method for the study of gas-surface interactions, the modulated molecular beam-mass spectrometric technique² was developed in this laboratory with Air Force Materials Laboratory sponsorship. This unique apparatus allows reactions between a heated solid material and discrete, controlled pulses of the reactant gas. Vaporizing reaction products are analyzed individually by the mass spectrometer. By synchronizing the spectrometer detection system to the vapor beam modulator, the periodic time-intensity waveform of each of the gaseous reaction products can be constructed, providing important information on the kinetics of the reaction under observation. The apparatus can also be operated as a conventional high temperature mass spectrometer system, providing a versatile tool for the study of several aspects of the vaporization process: vaporization, condensation, and reflection.

At the outset of this program, experimental data on graphite vaporization was confined to temperatures below 3000°K, where the equilibrium process seemed well established, but free vaporization, which is more closely related to the sublimation of material from heated re-entry vehicles, had received little attention. Therefore, the vaporization kinetics of graphite were very poorly understood, particularly with regards to polyatomic species in the vapor. In order to remedy this situation, a program to extend the range and nature of our experimental observations was created. This program, based on mass spectrometric study of the carbon vapors, includes: studies of free vaporization at temperatures to 3000°K and above, with special attention given to the detection of polymeric species of increasing size; experimental observations of vapor-surface interactions, specifically the reflection of carbon vapor by graphite surfaces; and the study of the nature of the carbon layers formed by condensation of carbon vapors on graphite substrates. The paragraphs below describe progress and accomplishments in this program.

II. CARBON VAPOR COMPOSITION

The composition of carbon vapor has been a subject of special importance for many years. The heat of vaporization of carbon atoms is a quantity basic to the thermochemistry of all carbon containing compounds. Yet this fundamental unit was not determined with certainty until the mid 1950's because the assumption of a monatomic character for the carbon vapor in equilibrium with graphite confused the interpretation of experimental data. Discovery of the polyatomic composition of this vapor was a major triumph of high temperature mass spectrometry.³⁻⁶ This effort culminated in the work of Drowart, DeMaria, Burns, and Inghram⁷, which established C_1 , C_2 , and C_3 as the three principal vapor phase species in equilibrium with graphite at temperatures up to 2700°K. Tetra-atomic and pentatomic species were also identified and heats of vaporization of C_1 , ..., C_5 were determined and have become the generally accepted values.

The inability to synthesize and isolate the individual C_n species makes experimental determination of the thermochemical properties of the larger species very difficult. This has prompted a number of theoretical studies of carbon vapor thermochemistry. The original work of Pitzer and Clementi⁸, which aimed at a complete calculation of the heats of formation and thermodynamic functions of all molecular carbon (C_n) species, predicted very high equilibrium partial pressures for C_n species of large n at high temperatures. These calculations were later modified by Strickler and Pitzer⁹ to accommodate the data of Drowart, et al⁷, but the conclusion remained that the very high temperature vapor composition contains significant amounts of large polymeric species. Other studies by Duff and Bauer¹⁰ and by Krieger¹¹ supported this view. Later theoretical calculations by Dolton, et al¹², and by Kratsch and co-workers¹³ were performed as part of larger efforts to predict graphite ablation behavior. These concur in predicting important contributions from large molecules at temperatures near 4000°K, although details in the results of the various calculations show considerable variance.

Although the temperatures of interest are above those conveniently obtained for conventional laboratory experiments, some evidence was uncovered supporting the expectation of large carbon vapor species. The results of Hintenberger, et al¹⁴ are representative of reports of a number of studies using a high frequency discharge between graphite electrodes. Ionized polymeric species as large as C_{31}^+ (for positive ions) and C_{33}^- (for negative ions) were observed by mass spectrometry. Using a pulsed laser beam to produce graphite vaporization, Berkowitz and Chupka¹⁶ observed neutral vapor species up to C_{14} by conventional mass spectrometry. However, the temperature or the extent of equilibrium is not well known for any of these experiments.

Knudsen-effusion mass spectrometric studies of graphite vaporization have now been extended to 3000°K. Wachi and Gilmartin¹⁷, Zavitsanos¹⁸, and Milne, et al¹⁹ have all employed Knudsen cells of pyrolytic graphite to study the equilibrium composition of carbon vapor. The largest polymeric carbon species detected by these observers were C_5 , C_4 , and C_7 , respectively. In this laboratory²⁰, we have used a Knudsen cell of

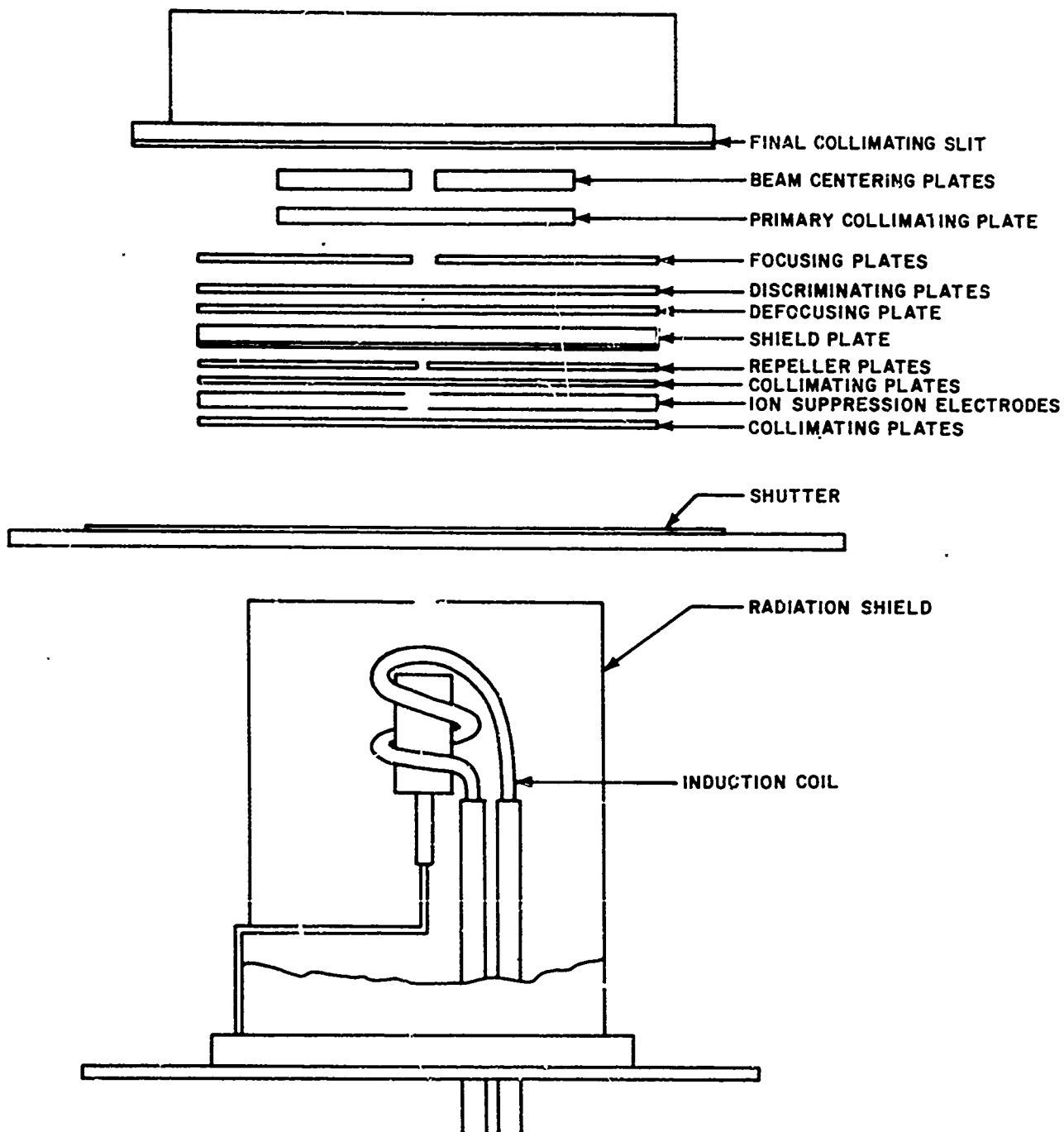
polycrystalline graphite in a thin-walled tantalum jacket and were able to detect C_6 and C_7 . Short cell life at $3000^\circ K$ prevented serious study of these polymers and limited our search for larger species.

Free vaporization of graphite is more pertinent to the ablation situation and its study is very important, since there is a real paucity of kinetic data for this system. Wachi and Gilmartin¹⁷ studied free vaporization from both pyrolytic and polycrystalline graphites, with interesting results. For pyrolytic graphite they were able to study C_4 and C_5 , but could detect no higher polymeric species, even though temperatures up to $3250^\circ K$ were attained. They studied several types of conventional polycrystalline graphites and were able to identify C_6 and C_7 in the vapor from these materials above $3000^\circ K$. An unusual time dependency in the ion ratios due to the various neutral polymeric species was observed also. In the laboratory, we were able to confirm the existence of a time dependency in the ion ratios. Our search for polymers in the free vaporization of polycrystalline graphite has led to the identification of all neutral species to C_{10} .

We have now repeated these measurements and extended them to higher masses in an attempt to verify the results of the previous study and to assess their importance. New procedures have been adopted and two new types of polycrystalline graphite have been examined, both resistive and inductive heating being employed.

The apparatus used for these experiments is the same as that described previously²⁰. It consists of a Nuclide HT-60 magnetic sector mass spectrometer fitted with a water cooled sample chamber which permits the graphite specimen to be held vertically beneath the ion source, with a line-of-sight path through the ion source into the analyzer region. This arrangement is depicted in Figure 1, which shows the inductive heating apparatus. The ion source and sample chambers are separately pumped and connected only by a slit in the movable shutter. For inductive heating, a 5 kilowatt RF generator is used to heat a cylindrical graphite specimen (0.25 inch diameter by 0.625 inch length). Temperature measurement is by optical pyrometry, with a black body hole (0.025 inch diameter by 0.15 inch deep) being drilled 0.1 inch below the top surface of the cylindrical specimen. For resistively heated samples, a graphite specimen (1.0 inch by 0.38 inch by 0.03 inch) is clamped between two water-cooled electrodes and suspended beneath the ion source. Temperature measurement is by optical pyrometry, but surface temperatures are measured and emissivity corrections made following Chang.²¹

In order to search for high molecular weight polymers vaporizing from graphite at temperatures near $3000^\circ K$, it has been necessary to modify our procedures. Previously we had degassed the specimen thoroughly at $2200^\circ K$ and then sought and verified each species above C_3 in sequence, advancing 12 mass units at a step. This resulted in increasing specimen deterioration as the polymer size increased, and experiments were commonly ended by an inability to continue heating to the required high temperature before the search had proceeded beyond C_7 or C_8 . Two other experimental features dictate special care and procedures. These are the very



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Figure 1 ION SOURCE AND HIGH TEMPERATURE CARBON SOURCE

temperature involved and the low level of the mass spectrometric signals to be detected. Both require a clean, thoroughly baked-out apparatus, since at these high temperatures adsorbed gases may be driven from walls to obscure the small amount of vaporizing polymer. Thorough degassing of the graphite specimen is required also. At 3000°K specimen deterioration is rapid and it is necessary to work quickly, even though the detection system time constant must be long to measure the weak ion signal. These limitations have led to adoption of the following procedures. After thorough bakeout and outgassing, the apparatus is allowed to cool. The graphite sample is heated to about 2400°K and the C₃ beam (mass 36) is used to adjust the mass spectrometer to focus species vaporizing from the graphite and discriminate against background gases. The ionizing electron energy is set for 17 eV and several points of I⁺ vs. T are determined for C₃ for calibration purposes. The magnetic field is then adjusted to focus at the mass of the parent ion of the highest polymeric species being sought--without recourse to our previous policy of seeking and verifying each species in sequence. The graphite specimen temperature is raised until a useful signal is recorded by the mass spectrometer. Three fairly rapid tests are then employed: the movable shutter is placed in the closed position and the signal change noted (but a complete shutter profile is not attempted); with the shutter open the ion source filament is turned off; and, with the shutter open and ion source on, the RF induction heater is abruptly shut off. Response to the first and third tests serve to distinguish true polymer vaporization from background, while the second test detects signals due to thermal ionization at the graphite surface. The temperature may then be raised and the sequence repeated. Tests are also performed on adjacent mass peaks to provide a behavioral comparison. Developing surface porosity, coatings on the RF induction coil and coatings on the optical viewing port all combine to limit the operating time available for a single graphite sample.

A typical background peak originating from hydrocarbon adsorbed on the vacuum chamber walls and desorbed by raising the operating temperatures will show no response to adjustment of the movable shutter. An abrupt drop in specimen temperature may elicit a response by the background peak, but it will consist of a slow drift to lower values and return to high specimen temperature will be accompanied by a correspondingly sluggish return in background peak intensity. Mass spectrometric signals due to carbon polymers vaporizing from the specimen surface will vanish when the movable shutter is closed and will drop abruptly with a sudden temperature drop and will be restored quickly upon renewed heating of the specimen. Furthermore, the minima attained by shutter or temperature drop will be approximately equal. When searching for the highest species (C₁₄, C₁₅) we were often unable to detect signals for peaks + 1 or 2 mass units from the selected peak using the same sensitivity settings yielding observable signals for this mass.

Results obtained for species larger than heptatomic carbon (C₇) are summarized in Table I and illustrated in Figure 2. Tests were performed on three kinds of commercial polycrystalline graphite: Aremco RG-504, Research Grade Graphite, Aremco Products, Inc., Box 145, Briarcliffe Manor, New York 10510; Poco Grade HPD-1 Graphite, Poco Graphite, Inc., P.O. Box 2121, Decatur, Texas 76234; and ATJ-S, Union Carbide Corp.,

TABLE I. Relative Intensities of Ions C_n^+

<u>n</u>	<u>T(°K)</u>	<u>I (C_n^+) x 10¹²</u>	<u>Specimen</u>
8	2860	0.07	RG-504
9	2890	0.03	RG-504
	2900	0.023	RG-504
10	2960	0.2	RG-504
	2980	0.09	RG-504
	2990	0.48	Poco
11	3000	0.037	RG-504
14	2850	0.25	RG-504
	2850	0.1	ATJ-S
	2880	0.25	Poco
	2900	0.3	ATJ-S
	2910	0.045	RG-504
	2930	0.1	RG-504
	2950	0.3	Poco
15	2940	0.007	RG-504

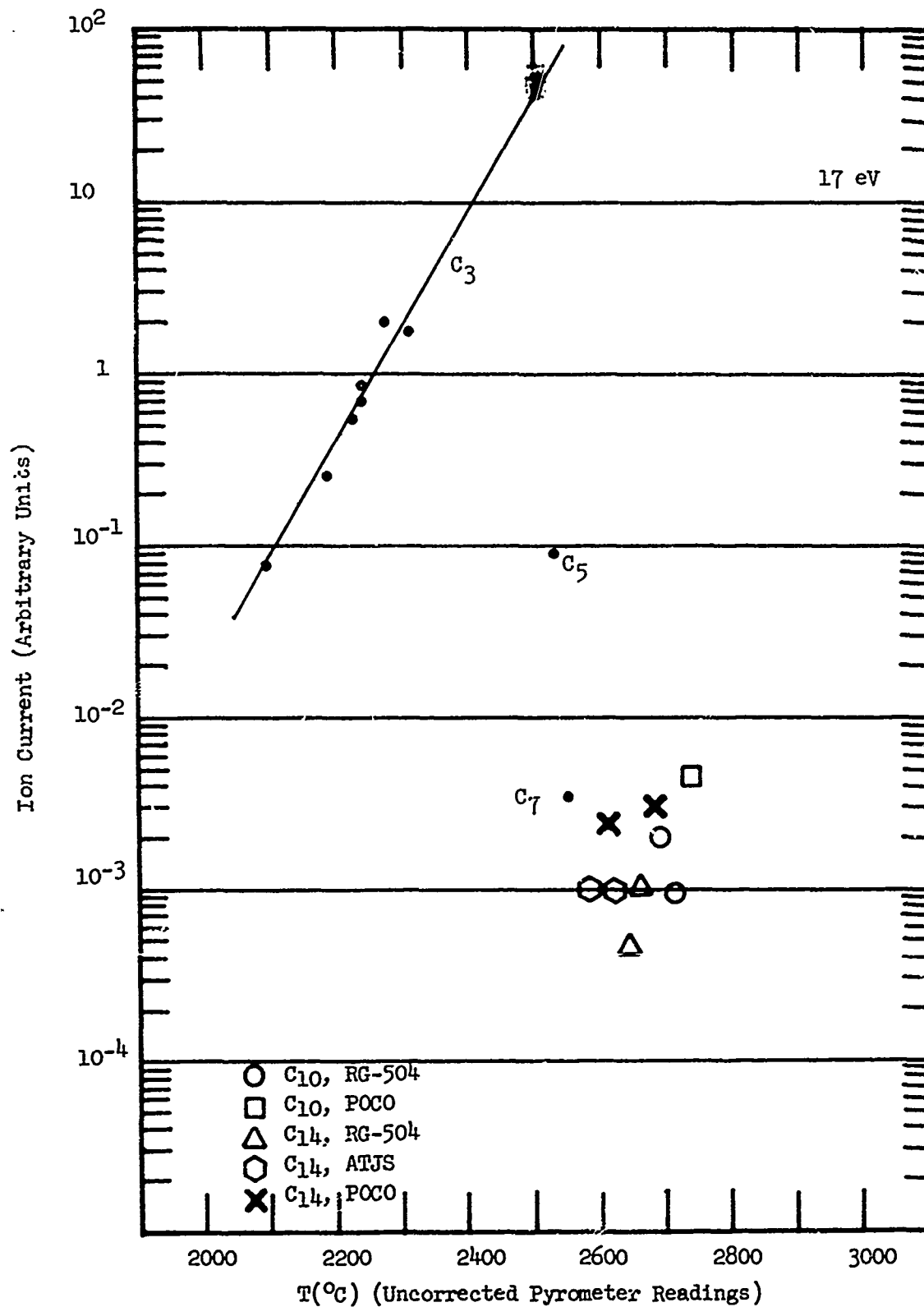


Figure 2. Carbon Vapor Composition

Carbon Products Division, 270 Park Avenue, New York, N.Y. 10017. All three materials have produced mass spectrometric signals identified as originating from vaporizing molecules of C_{10} and C_{14} . In addition to the data of Table I, all of which was obtained by induction heating and using low ionizing electron voltages (17 eV) in the mass spectrometer, we have performed two other experiments. In the first of these, we have used high voltage (100 eV) ionizing electrons to locate vaporizing species and have identified signals at $m/e = 144$ (C_{12}^+) as originating from material vaporizing from the graphite specimen. Secondly, using low electron voltages (17 eV), but using resistive heating, we have obtained confirmation of our above results for C_{10} and C_{14} . At temperatures of $2850 \pm 50^\circ K$, we have obtained mass spectrometric signals for both species with intensities comparable to those listed in Table I. Attempts by both methods to detect C_{18} were unsuccessful.

Perusal of the data of Table I reveals considerable scatter in the ion intensities observed for a given species. Furthermore, no discernible trend with temperature exists. Several possible explanations can be set forth to account for this behavior. The high overall rate of vaporization of graphite at the high temperatures used in the polymer search (to $3000^\circ K$) results in rapid build up of a coating on the glass window of the optical viewing port used for temperature measurement by optical pyrometry. Accurate correction for coating absorbance cannot be made with conditions changing this rapidly. A more serious source of uncertainty lies in the changing surface morphology of polycrystalline graphites under vaporizing conditions. These conventional graphites are manufactured to contain a crystalline filler phase and an "amorphous" binder phase. The two phases may vaporize at different rates producing a porous surface. This situation has been described by Kratsch, et al¹³, and has been invoked by Wachi¹⁷ as a partial explanation of their observed time dependency of ion intensities of C_1^+ , C_2^+ , and C_3^+ in vaporization from polycrystalline graphite. In this laboratory we have also observed a time dependency of ion intensities and have documented the increase in surface porosity under vaporizing conditions. These pores may act to some extent as small effusion cells, with steady-state partial pressures of the various carbon species approaching their equilibrium vapor pressures. This could have a pronounced effect on the observed vaporization rate of those species with low vaporization coefficients. Since the polymeric carbon species are suspected of having very low vaporization coefficients, the partial equilibrium situation of the porous surface would result in an apparent enhancement in relative abundance of these species in the vapor. Differing degrees of porosity from sample to sample, depending on graphite type and high temperature history, would produce variation in experimental I^+ vs. T data and, in any case, the effects of vaporization kinetics would be disguised.

In spite of these complications, it is interesting to compare our results with past data and with the predictions of the theoreticians. For example, the calculations of Kratsch, et al¹³, employing carbon vapor species of linear structure only, predict a partial pressure for C_{10} at $3000^\circ K$ which is approximately six orders of magnitude less than the partial pressure of C_3 at that temperature. When ring structures are included, a slightly higher partial pressure is predicted for C_{10}

at 3000°K, but the importance of ring structures is said to diminish at higher temperatures. This calculation is in close accord with our experimental results for C₁₀. The calculated partial pressure of C₁₄ for either rings or chains is lower than we observe. Hoffmann²² has performed calculations based on extended Huckel theory which predict rings to be more stable than chains for carbon polymers C_n with a periodicity $n = 4q + (q \geq 2)$. Thus, both C₁₀ and C₁₄ are predicted to be more stable as rings than chains, but Hoffmann made no attempt to calculate abundances in the vapor. It is interesting to note that the ring structures referred to are simple polygons. Polycyclic fragments of a graphite lattice, with shapes similar to anthracene, etc., are very unstable relative to simple polygons with the same number of carbon atoms.

In addition to polymeric ions formed in arcs, the vapor formed by laser heating of graphite was shown by Berkowitz and Chupka¹⁶ to contain significant amounts of C₁₀ and C₁₄. Indeed, the calculations of Kratsch, et al predict C₁₄ to be the second most important carbon species (second to, but far below C₃) in the chemical composition of an ablated mass of carbon (100 atm., 7800°R). Our own experiments extend only to 3000°K, but experiments using resistive heating commonly end in burn-out of the graphite specimen. At the latter condition, strong signals saturating the electrometer are obtained for all species studied, including mass 168 (C₁₄). Experimental observations at higher stable temperatures, such as might be attained with continuous laser heating or by bombardment with focussed electron beams, should provide valuable data on this subject.

III. THE MASS SPECTRUM OF C₃

Identification of neutral vapor species is an important step in the mass spectrometric study of high temperature vaporization. When the vapor consists of one or more polyatomic species, the mass spectrum of the vapor will be a composite of ions formed by simple ionization of the neutral molecules and those formed by electron impact dissociation of the parent ion. However, it is difficult to determine the characteristic fragmentation pattern for molecules in vapors from condensed phases since these vapors usually have several components and it is not possible to synthesize and isolate the individual species. Ionization efficiency curves of each ion are examined to provide information as to its origin (parent ion or fragment), and the vaporization data is taken with an ionizing electron voltage chosen to minimize (or eliminate) contributions from fragment ions to the mass spectrometric signal at the mass of interest. This procedure was followed and 17 eV was selected as an optimum ionization voltage for study of carbon vapors; this is approximately 5 volts above the threshold of 12 eV of the ionization efficiency curves for C₁⁺, C₂⁺, and C₃⁺.

Experiments on the reflection of carbon vapors by graphite surfaces have provided an unusual opportunity to study the triatomic carbon vapor species (C₃) in relative isolation. Although all three major carbon vapor species (C₁, C₂, and C₃) are condensible and are not permanent gases at the temperature of the vacuum chamber walls and ion source plates, we have shown previously that C₃ is selectively reflected from

graphite surfaces held at temperatures near 1000°K (see Figure 3 below). The effect of electron impact fragmentation is readily observable in our reflection measurements. At 20 eV the curve of reflected C_1 (atom) intensity as a function of reflecting surface temperature follows the course outlined in Figure 3. At 25 eV, a large electron impact fragmentation contribution at mass 12 causes the apparent observed C_1 reflection to behave in the manner depicted for C_3 .

We have performed a simple experiment in which the ion currents at masses 12, 24, and 36 were recorded at 100 eV for the reflected carbon vapor beam at constant beam intensity and reflecting surface temperature $T_s = 1000^\circ\text{K}$). The observed values are due almost entirely to C_3 ionization and fragmentation, but small corrections for contributions from atomic or diatomic vapor species are made by estimating the maximum possible contribution from the measurements performed at 17 eV and the known appearance potential curves. The resulting pattern gives the ratio $C_3^+/C_2^+/C_1^+$ as 100/2.1/2.9. This is given in Table II as percentage of total ionization and is compared to the mass spectra of several C_3 hydrocarbons, with all ions containing a given number of carbon atoms being listed as a single sum. It is interesting to note the similarity of the C_3 spectrum with that of propyne (C_3H_4) when hydrogen atom dissociation is ignored.

TABLE II. Mass Spectra of C_3H_x Hydrocarbons (70 eV)

	<u>C_3</u>	<u>$C_3H_4^*$</u>	<u>$C_3H_6^*$</u>	<u>Cyclo-$C_3H_6^*$</u>	<u>$C_3H_8^*$</u>
CH_x	2.8	2.3	3.2	3.9	2.9
C_2H_x	2.0	2.8	13.8	13.4	64.7
C_3H_x	95.2	94.9	79.8	79.8	30.8

*From Mass Spectra Data, API Research Project 44.

IV. CARBON VAPOR REFLECTION BY GRAPHITE

Understanding the kinetics of graphite vaporization requires experimental data on all the various aspects of this vaporization-reflection-condensation phenomenon. Mass spectrometric data has been used by Thorn and Winslow²³, by Burns, Jason, and Inghram²⁴ and by Zavitsanos²⁵ to determine vaporization coefficients of the principal species over graphite. Although agreement is only approximate, the three studies coincide in yielding vaporization coefficients for C_1 and C_2 of between 0.14 and 0.5, while the value for C_3 is smaller by nearly an order of magnitude. Hoch and co-workers²⁶ are currently employing an isotopic exchange technique with a triple Knudsen cell to measure individual condensation coefficients of the carbon vapor species. Direct observation of carbon vapor reflection by graphite surfaces is limited to the single study by Chupka, Berkowitz, Meschi and Tasman²⁷. In 1962 they reported the results on an experiment in which a mass spectrometer was

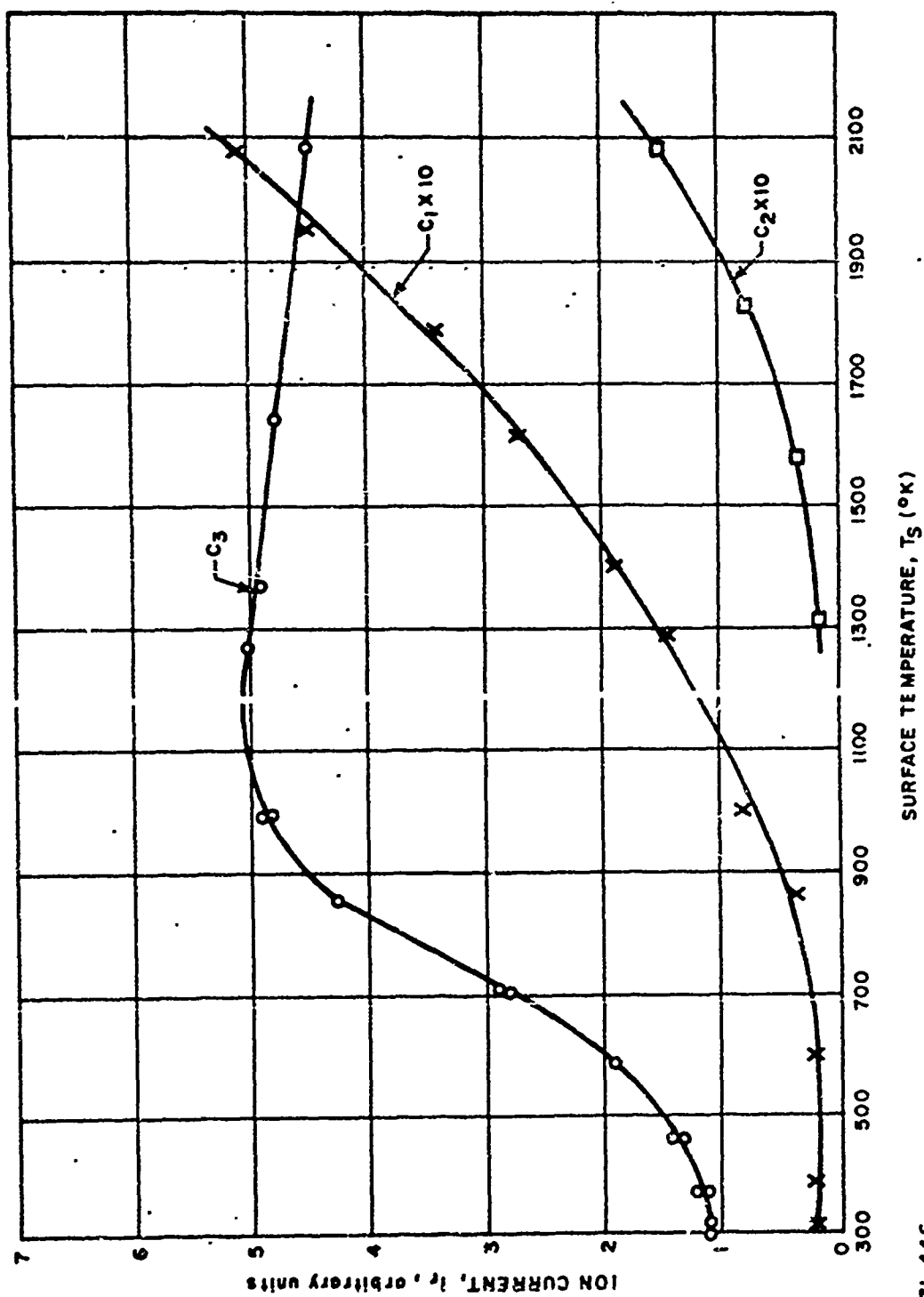


Figure 3. C_3 REFLECTION FROM POLYCRYSTALLINE GRAPHITE

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used to detect carbon vapor reflected from a graphite filament. Two parallel 0.020 inch graphite filaments were suspended under the ion source of a mass spectrometer in such a way that only one filament was "visible" via line-of-sight path to the ionizer. A portion of the atoms or molecules vaporized or reflected from this filament could be analyzed and detected by the mass spectrometer. Measurements were made to compare ion intensities of each species produced by direct evaporation from the visible filament with those produced by evaporation from the other filament and reflection from the surface of the visible filament. Values for a reflection coefficient α_r (number reflected/number impinging) were calculated assuming a random distribution for the reflected beam. Results were reported for C_1 and C_3 only, and for only two values of the temperature of the reflecting surface. These interesting observations gave: for C_1 , $\alpha_r = 0.3 \pm 0.15$ ($T = 800^\circ\text{K}$) and $\alpha_r = 0.6 \pm 0.2$ ($T = 2300^\circ\text{K}$); for C_3 , $\alpha_r = 1.1 \pm 0.2$ ($T = 800^\circ\text{K}$), and $\alpha_r = 0.9 \pm 0.2$ ($T = 2300^\circ\text{K}$).

The study of carbon vapor reflection by graphite surfaces comprises an important part of the present investigation of graphite vaporization kinetics. Recently we have adopted our modulated beam mass spectrometer to a study of carbon vapor reflection²⁰. Operating primarily without beam chopping, we have verified qualitatively the results of Chupka, et al²⁷, and have greatly extended their study by including C_2 and by providing a continuous record of reflection as a function of target temperatures in the region $300^\circ\text{K} < T_s < 2100^\circ\text{K}$. These results are depicted in Figure 3. The upper temperature limit of 2100°K was imposed by target vaporization which obscured the reflected beam above this point. Temperatures of both the target and the vapor beam source are determined by optical pyrometry. Since carbon vapor is condensible and pumping is not a problem, both slits S_1 and S_2 (Figure 7) have been widened. An optical viewing port is placed such that the temperature of the back side of the target can be read and, looking past the target, the vapor source can be viewed through slits S_1 and S_2 . As we described previously²⁰, comparison of reflected beam intensity with the intensity of the beam formed by target vaporization when the target temperature is set equal to the beam source temperature, permits calculation of a reflection coefficient α_r for the vapor species being examined. Unfortunately, the quality of the temperature comparison is not perfect since the source temperature must be viewed through slits and two surfaces of varying roughness are being compared. Therefore, the value of α_r is uncertain by ± 0.1 . The ordinate in Figures 3, 5, 6, and 8 is given as the ion current of the reflected beam in arbitrary units. However, as discussed previously²⁰, our calculations plus the lack of an observed condensate for C_3 above $T_s = 1000^\circ\text{K}$, leads us to assign a value of $\alpha_r = 1$ to C_3 above this temperature. The slight enhancement in C_3 ion current with decreasing surface temperature may indicate partial thermal accommodation of the C_3 kinetic energy. For a typical experiment, the ion currents of approximately 10^{-17} amps are observed for C_3 at the mass spectrometer detector.

In order to extend our measurements to $T_s > 2100^\circ\text{K}$, we have used beam modulation to provide discrimination between the reflected beam

(modulated) and the vaporizing surface (non-modulated). The apparatus is then used as depicted in Figure 4 and also with a Princeton Applied Research Corp. lock-in amplifier (Model JB-5) replacing the digital signal averager. We have chosen to operate at a chopping frequency of about 40 cycles per second with the beam source operated at near 2700°K. Typical results are shown in Figures 5 and 6. The intensity of the reflected C₃ beam is seen to continue to decrease slightly with increasing surface temperature to 2600°K. The intensity of the reflected carbon atom beam increases as T_s increases to 2600°K. Pulse shapes as obtained on the digital signal averager continue to faithfully reproduce the chopper profile, showing no observable surface residence time for the vapor beam. These results show a continuation of the trends previously observed at lower temperatures.²⁰

Above 2600°K (T_s) the situation changes dramatically. The lock-in amplifier output becomes wildly erratic and the digital signal averager is no longer able to construct a satisfactory waveform. The reason for this behavior is not clear. As this upper temperature limit is approached, the signal to noise ratio approaches 10⁻³, a level which should not incapacitate our signal extracting system. The effect is reproducible and does not seem to be dependent on the absolute level of ion current reaching the mass spectrometer detector. Possible explanations include gas phase scattering or important gas-surface interactions. It is the latter phenomenon which was being sought, and, if this is an important effect, then further progress in these studies depends on the use of isotopically labelled materials. If the incident molecular beam has an isotopic composition different from that of the target surface, then a comparison of isotopic composition of the incident and reflected beams will provide a direct determination of the degree of chemical interaction of the incident beam and the surface. Subsequent paragraphs will describe preparation for and execution of a set of experiments in which the molecular beam of carbon vapor is enriched in the 13C atom concentration.

A. Carbon Vapor Sources

The molecular beam of carbon vapor required for the reflection experiments is obtained by heating specially prepared graphite sources. The most commonly used source consists of a solid graphite rod encased in a tantalum tube of 0.1 inch inner diameter. As is shown in Figure 7, this cylinder is mounted horizontally in an RF induction coil inside the vacuum system. When heated to about 2700 K, the carbon atoms and molecules evaporating from the front surface of the graphite cylinder provide a carbon vapor beam of sufficient intensity for ready detection after reflection from the target surface. The purpose of the tantalum sleeve is to act as an RF susceptor and to shield the coils from direct exposure to the rapidly vaporizing graphite surface.

Power limitations (only a 5 kilowatt RF generator was conveniently available) and the geometry of existing equipment have dictated our approach to the induction heating methods used in this program. It has been necessary to place the induction coil inside the vacuum system and we have followed three general principles to obtain maximum efficiency. These are: keep the leads between the RF generator and the induction coil as short as possible; keep the leads as close together as possible throughout their entire length, including the point at the vacuum feed-

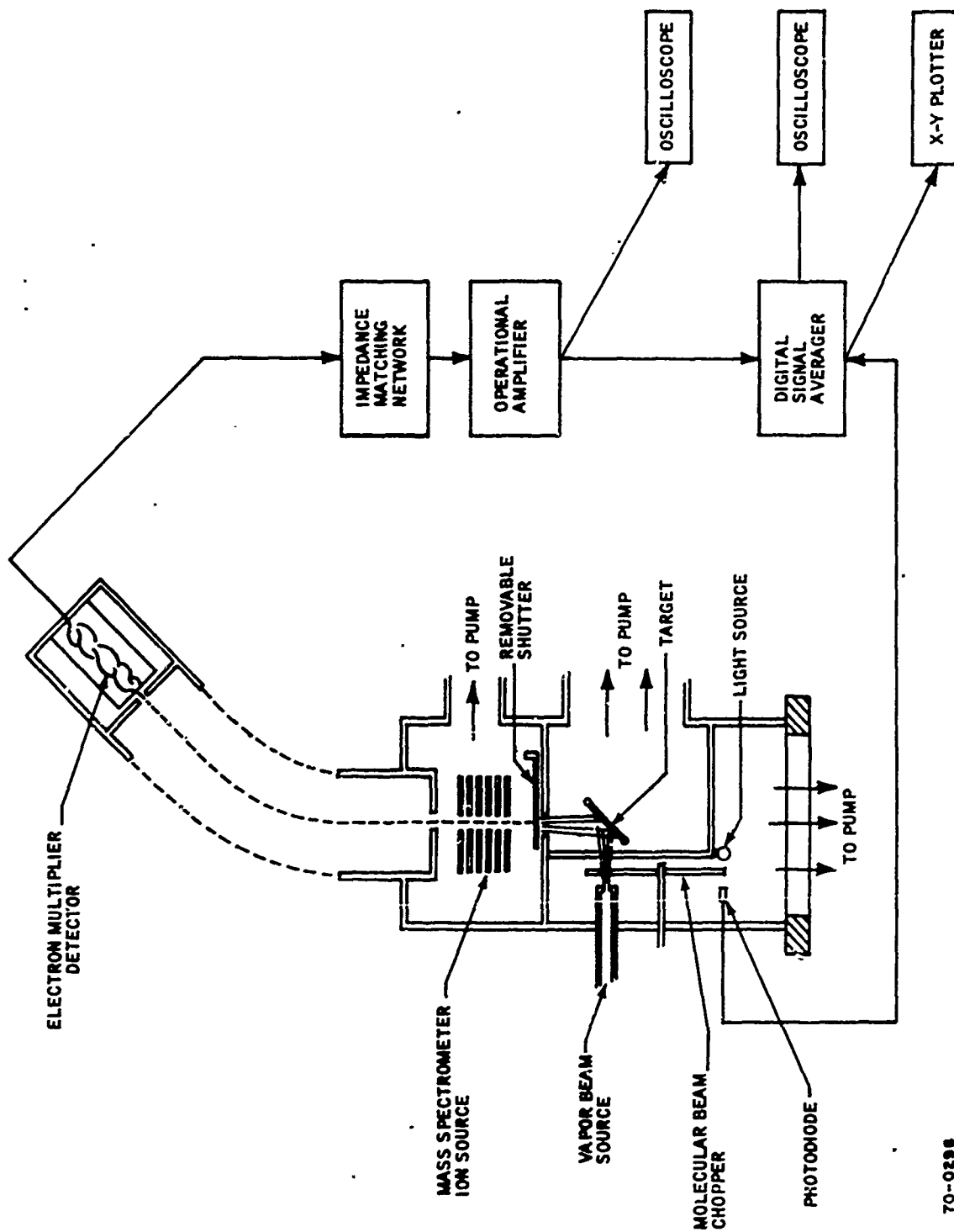


Figure 4. SCHEMATIC DIAGRAM OF AVCO'S PULSED MOLECULAR BEAM MASS SPECTROMETER

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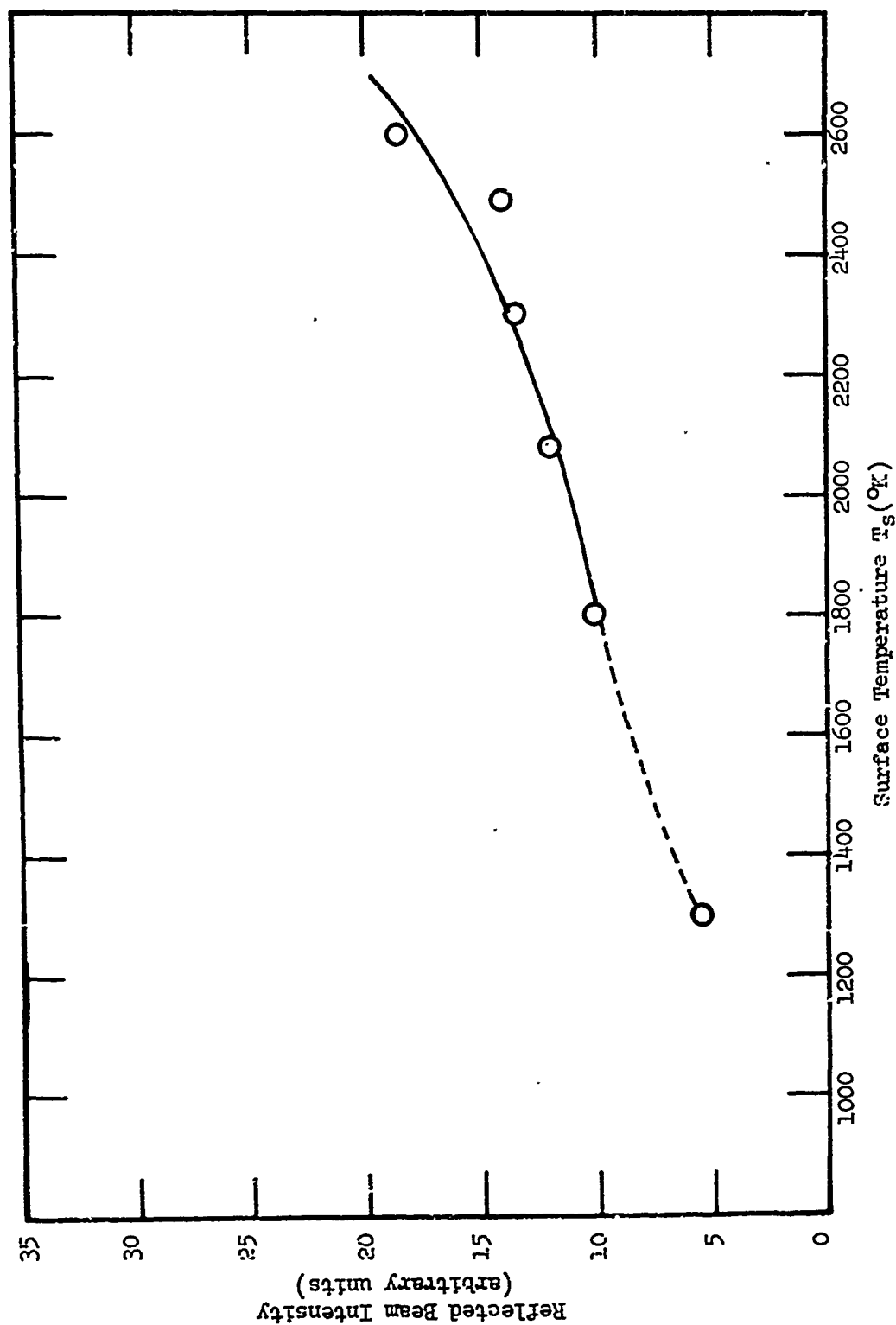


Figure 5. Carbon Atom Reflection

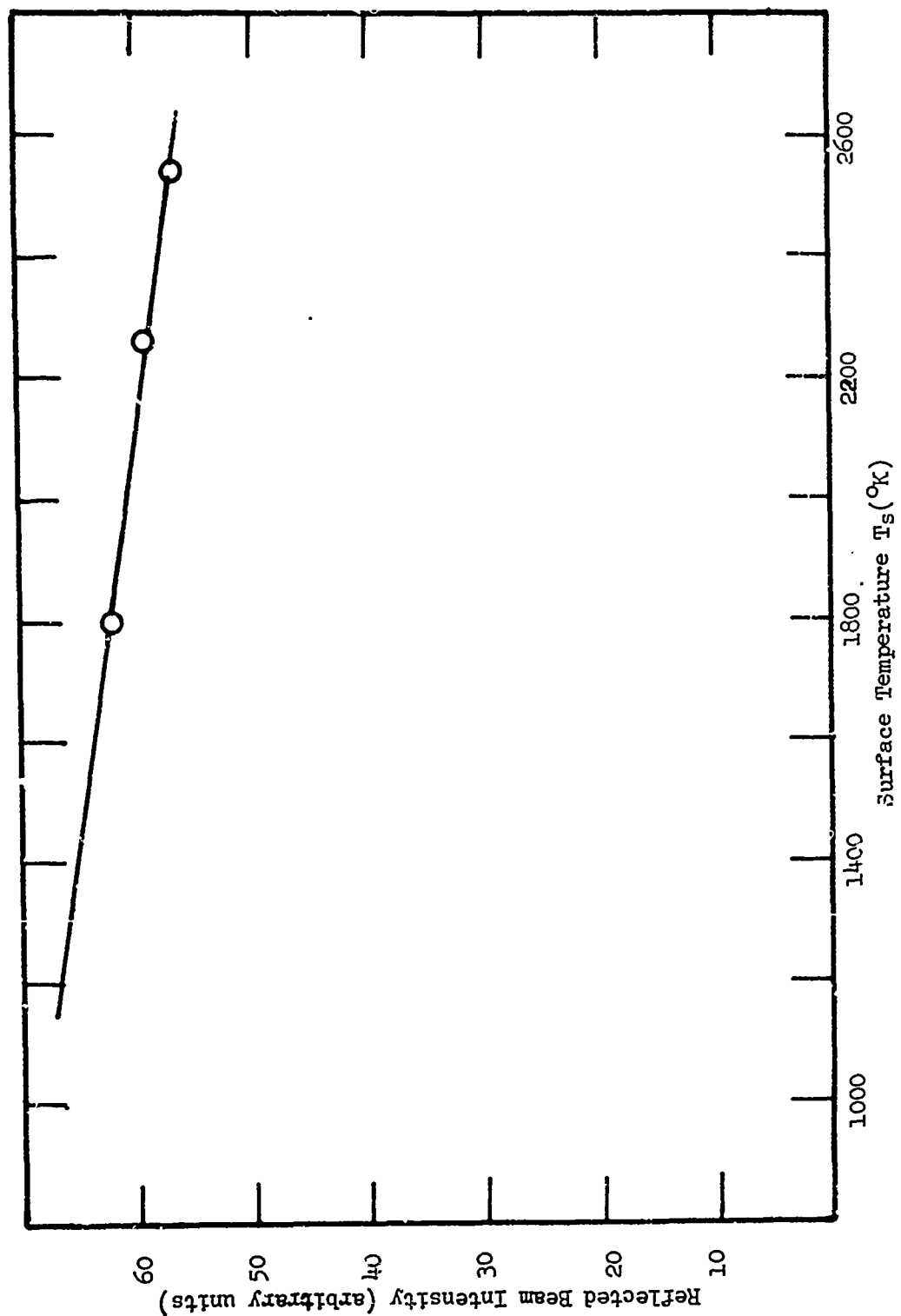
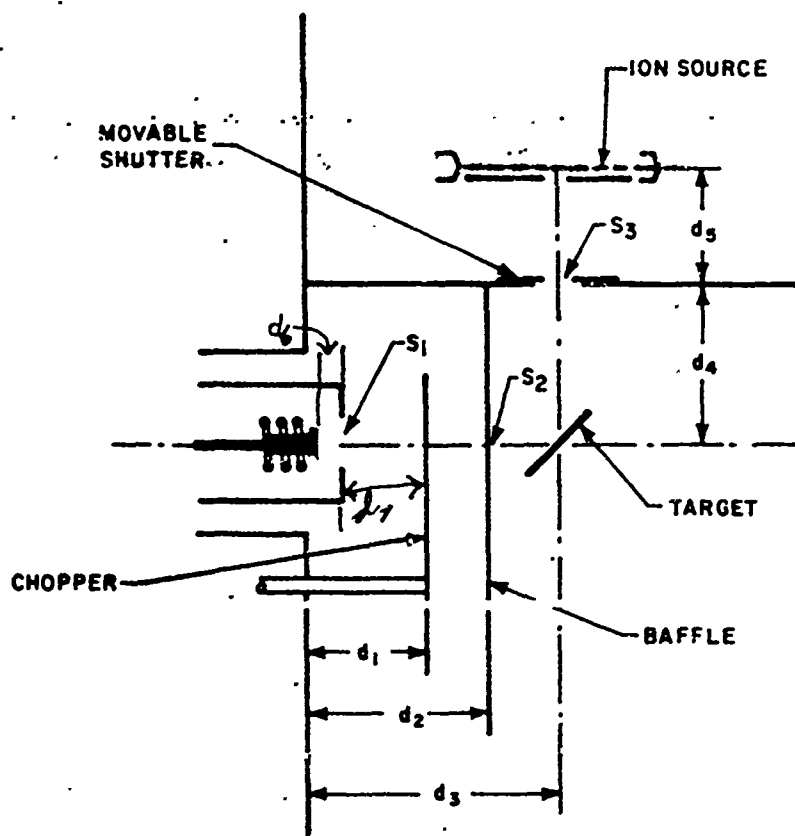


Figure 6. C_3 Reflection



$S_1 = ? \times ?$

$S_2 = ? \times ?$

$d_6 = ?$

$d_7 = ?$

$d_1 = 3.4 \text{ cm}$

$d_2 = 5.5 \text{ cm}$

$d_3 = 7.5 \text{ cm}$

$d_4 = 3.2 \text{ cm}$

$d_5 = 3.2 \text{ cm}$

$S_3 = 0.5 \text{ cm} \times 0.1 \text{ cm}$

TARGET $2.5 \text{ cm} \times 0.4 \text{ cm}$

SOURCE $0.25 \text{ cm} \times \text{RADIUS} - S_1 ?$

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Figure 7 DETAILS OF MOLECULAR BEAM REFLECTION APPARATUS

distances from source to various slits & to target, surface should be specified

*(location)
Ports 1 & methods for measuring vapor source & target temperatures should be specified.*

through; and have the induction coil as close to the specimen surface as possible. Centering the specimen within the coil is very important. Applying these principles to our beam source construction has resulted in a unit using leads (of 0.25 inch O.D. copper tubing) approximately 12" long. The three turn induction coil is of 0.125 inch copper tubing wrapped in a coil of 0.3 inch inner diameter. The graphite source described above is centered in this coil and can be heated to 2700°K using about 65% of the available power from the 5 kilowatt generator. The exact power temperature relationship is very sensitive to placement of the specimen within the coil.

Isotopically enriched carbon ($\sim 92\% \text{ }^{13}\text{C}$) is available commercially only as a fine grained graphite powder*. Since our experience has been that this powder cannot be compacted into a useful rod without inclusion of an undesirable binder material, we have developed a new source using the same tantalum tubing used as the sleeve in our other sources. One end of this tube is crimped to produce a very narrow slit 0.15 inch high. The tube is filled with graphite powder and set on a base of graphite rod. This source is heated by RF induction with the graphite rod base slightly outside the RF coil. An intense carbon vapor beam is produced by heating to the 2700°K region, with the intensity and useful lifetime perhaps even surpassing that of the original source made of rod only. Table III shows the isotopic composition of a carbon vapor beam from the enriched powder in comparison with that from a source of normal isotopic composition. Overlapping of the two spectra is seen to diminish as the number of carbon atoms increases, since for natural carbon $I^{+13}\text{C}/I^{+12}\text{C} \approx 1/10^2$ $I^{+13}\text{C}_3/I^{+12}\text{C}_3 \approx 1/10^6$. Thus, the $^{13}\text{C}_3$ (mass 39) in the isotopically enriched beam can be seen in reflection without significant interference from a rapidly vaporizing target surface. It may be noted that for the case of equal target and beam source temperatures, simple geometrical considerations predict a mass spectrometrically observed target vaporization to reflected beam signal ratio of about 10^{+3} (cosine distribution and unit reflectivity assumed).

Use of this source in our reflection experiments requires that we obtain a direct measure of the composition of the vapor emanating from it under actual experimental conditions. To accomplish this, the apparatus of Figure 1 was used and the vapors were sampled directly by the mass spectrometer. The results are summarized in Table IV. In addition to the main molecular beam of carbon vapor emerging from the source slit, a profile obtained with the movable shutter revealed a sizeable component of the carbon atom beam to originate on the tantalum (carbide) surface alongside the slit. No appreciable side component was observed for C_2 or C_3 . The possibility that the carbon atoms of the side beam had diffused through the tantalum tube wall suggested the development described below.

B. Carbon Atom Source

In an attempt to obtain a carbon vapor beam composed solely of

*X-ray diffraction measurements show that this powder is not amorphous, but is a crystalline graphite.

TABLE III. Isotopic Composition of Carbon Vapor Species

<u>Species</u>	<u>m/e</u>	<u>Normal %</u>	<u>Enriched %</u>
^{12}C	12	98.931	8.2
^{13}C	13	1.069	91.8
$^{12}\text{C}_2$	24	97.873	0.67
$^{12}\text{C}^{13}\text{C}$	25	2.115	15.06
$^{13}\text{C}_2$	26	0.0114	84.27
$^{12}\text{C}_3$	36	96.823	0.055
$^{12}\text{C}_2^{13}\text{C}$	37	3.139	1.85
$^{12}\text{C}^{13}\text{C}_2$	38	0.0339	20.73
$^{13}\text{C}_3$	39	0.000122	77.36

TABLE IV. Vapor Composition from Tube Furnace(T = 2650°K)

<u>Species</u>	<u>I(C_n⁺)</u>
C ₁	{ 100 slit 320 side
C ₂	{ 30 slit 3 side
C ₃	400 slit only

carbon atoms, the slit of a tantalum tube furnace previously described herein was welded shut using an electron beam welder. The tube was packed with graphite powder and otherwise treated in the same manner as the previous source. Composition of the vapor beam detected by the mass spectrometer upon heating this source to 2650°K is tabulated in Table V. A beam containing over 99% carbon atoms was obtained. This source offers some important new advantages for study of carbon vapor-graphite surface interactions. In particular, it affords the opportunity to study atom combination reactions at the surface as well as to study atom reflection unperturbed by co-existing molecular species.

TABLE V. Vapor Composition from Atom Source

<u>Species</u>	<u>I (C_n⁺)</u>
C ₁	100.
C ₂	1.0
C ₃	0.2

C. Reflection of Isotopically Labelled C₃

For standard reflection experiments, beam modulation is not employed. With both shutter and chopper in the open position, the vapor source temperature is adjusted so as to provide a mass spectrometer ion current for the desired species of satisfactory intensity. The vapor beam is then interrupted by rotating the chopper wheel to the closed position. The target surface is then cleaned by "flashing" the target to above 2500°K for a time (approximately 1 minute) sufficient to vaporize all condensed carbon or other gases, as well as several atomic layers of the target material itself. The cleaning process can be followed by monitoring the vaporizing species with the mass spectrometer. When the cleaning process is complete, the target is suddenly reduced to the temperature of the experiment (water cooled electrode in the target holder accelerate the rate of target temperature adjustment) and the chopper wheel is rotated to the open position within 10 to 20 seconds. The reflected beam intensity is then measured. This procedure is repeated for each data point.

Use of isotopically labelled carbon vapor beams is only slightly more complicated. If there is no interaction (other than simple reflection) between the carbon vapor beam and the graphite surface, then the isotopic composition of the reflected beam will be unchanged from that of the incident beam. If, on the other hand, the gas-surface interaction includes any process involving interchange of gas and surface atoms, then the isotopic composition of molecules in the reflected beam will differ from that of the incident beam. Concurrently, any process leading to such an interchange, or to condensation, will contribute to an alteration of the isotopic composition of the target surface. The surface can be restored to normal composition by blocking the beam with the chopper wheel and holding the target at a high vaporizing temperature until the observed

isotope ratios in the vapor indicate that all excess ^{13}C has been removed. Our experience has been that the condensed material is removed quickly by flash vaporization, and our observations of the isotopic composition of this flash desorbed material, as is described later, sheds some light on interactions in the condensed phase.

Two types of measurement have been performed to study the interaction of the triatomic portion of the isotopically labelled carbon beam with the graphite surface. First, following earlier procedures, we have monitored the intensity of the reflected $^{13}\text{C}_3$ beam (mass 39) as a function of target temperature. These results duplicate those from our earlier studies with beams of normal isotope concentrations for target surface temperatures below 2100°K . In addition, we were able to extend these observations to target temperatures up to 2800°K without recourse to beam chopping. These results are depicted in Figure 8. The reflected $^{13}\text{C}_3$ beam intensity shows no dramatic change as the target temperature approaches and then exceeds the beam source temperature ($T_B = 2650^\circ\text{K}$). The general trend to slightly lower reflected beam intensities continues as the target temperature is raised from $T_S = 1000^\circ\text{K}$ to 2100°K and on to $T_S = 2800^\circ\text{K}$.

The ratio of $^{13}\text{C}_2^{12}\text{C}$ (mass 38) to $^{13}\text{C}_3$ (mass 39) in the reflected beam is also a sensitive measure of the beam-surface reaction. For no interaction the ratio should remain unchanged, but if the gas-surface interaction includes any process involving interchange of gas and surface atoms, then the relative amount of $^{13}\text{C}_2^{12}\text{C}$ will be enhanced. Table VI shows the ratio, R , of mass 38 to mass 39 for several target surface temperatures ranging from $T_S = 1350^\circ\text{K}$ to $T_S = 2670^\circ\text{K}$. Within experimental error, the value of R is constant for all T_S and is equal to R of the incident beam.

These two experiments indicate that there is no interaction between beam molecules and surface atoms. Furthermore, we were able to detect no time dependency in either the isotope ratio or absolute intensities of the $^{13}\text{C}_3$ molecules in these reflection experiments, which indicates no interaction takes place on the surface despite growing changes in surface isotopic composition due to condensation of $^{13}\text{C}_1$ and $^{13}\text{C}_2$ on the target. This, together with our inability to detect a surface residence time for C_3 , leads us to conclude that no adsorption interaction takes place. The observed slight trend to higher observed intensity of reflected C_3 as the surface temperature is lowered from 2800°K to 1000°K may be attributed to partial accommodation of C_3 translational energy by the target. This would decrease the translational velocity of the reflected beam, producing a longer transit time of the molecule through the ion source, with a corresponding increase in the probability of ionization.

V. CARBON VAPOR CONDENSATION AND FLASH DESORPTION

Although C_3 is totally reflected for target surface temperatures above 1000°K , a large fraction of this species condenses on the surface at 800°K and below, and C_1 and C_2 are condensed throughout the complete range of surface temperatures. The fate of these species is the subject of this section.

We have described previously²⁰ the results obtained when a thin film of vapor deposited carbon is desorbed by an abrupt jump in the temperature

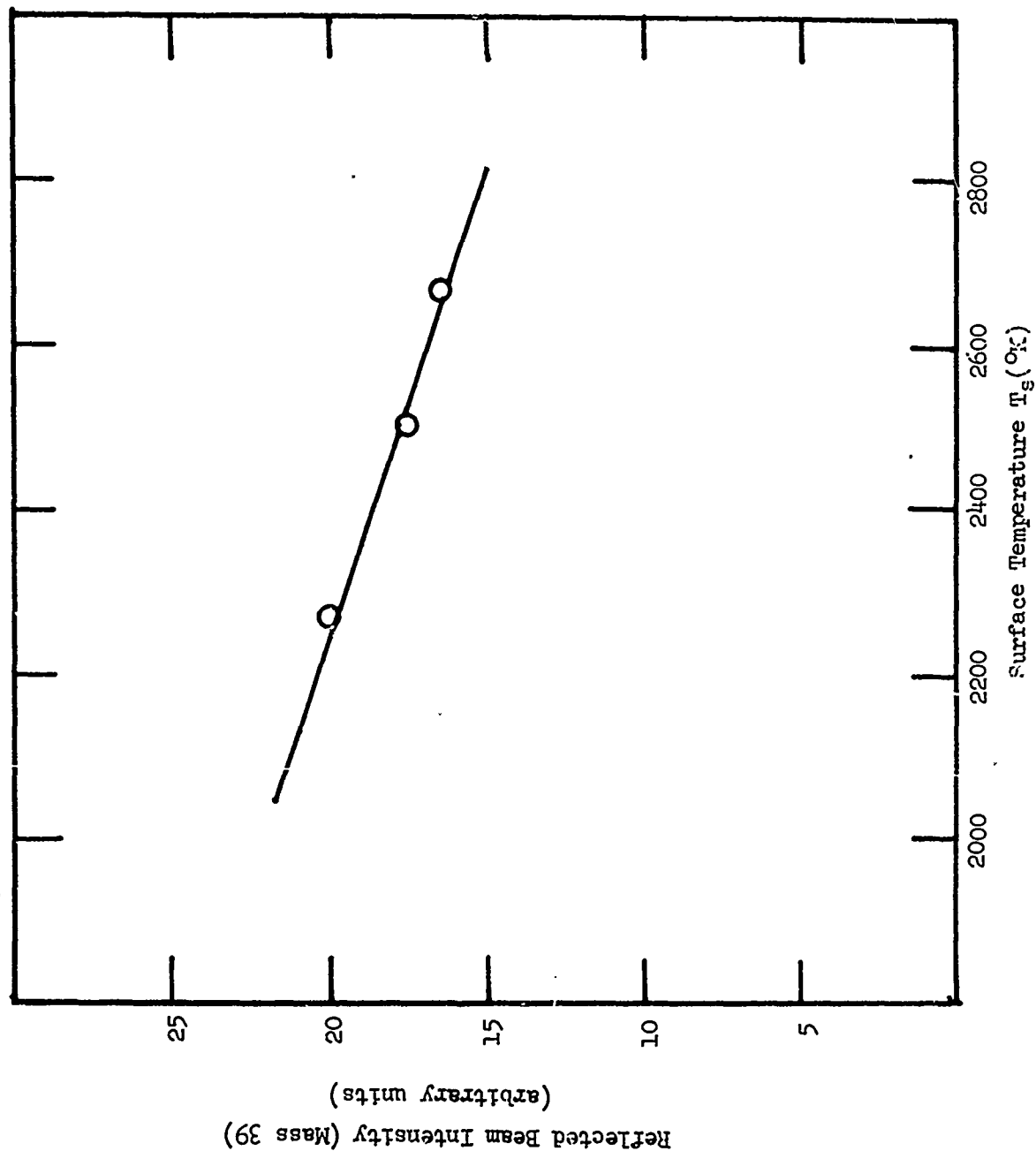


Figure 8. $^{13}C_3$ Reflection

TABLE VI

Reflection of Isotopic Varieties of C₃

<u>Run</u>	<u>T_B(°K)</u>	<u>T_S(°K)</u>	<u>R ($\frac{\text{Mass } 38}{\text{Mass } 39}$)</u>
a	2550	1760	0.29
a	2550	2320	0.29
a	2550	2520	0.28
b	2600	1350	0.27
b	2600	2270	0.28
b	2600	2500	0.28
b	2600	2670	0.25
	Calculated		0.268

of the solid surface. Flash vaporization of the carbon layer condensed on a tungsten ribbon substrate results in formation of a vapor composed solely of carbon atoms. When the solid substrate is a room temperature polycrystalline graphite (RG-504) target, the "flashed" vapor contains the three major species C_1 , C_2 , and C_3 . On the other hand, if the polycrystalline graphite target is maintained above 1100°K during the carbon vapor deposition period, no C_3 is flash vaporized by sudden heating of the target to 2600°K . Experimental observations of the two cases involving a graphite substrate differ in the path of approach of C_3 vaporization rate to the normal free vaporization rate of that species from the clean surface. Flash heating the specimen held at $T_s > 1100^\circ\text{K}$ produces a steady increase in the C_3 vaporization rate which gradually approaches the normal rate, while similar treatment of the specimen held at room temperature during condensation results in an initial burst of C_3 vaporization which then falls to the lower normal vaporization rate characteristic of the substrate. For carbon atom vaporization, initial bursts are recorded for both conditions.

The failure of polycrystalline graphite surfaces held at $T_s > 1100^\circ\text{K}$ during the deposition process to produce a C_3 burst during flash vaporization (C_1 is flash desorbed) can be attributed to the total reflection of C_3 by the target surface. It also indicates that C_3 is not formed by collisional processes from mobile carbon atoms on the surface. When the target surface is kept at lower temperatures during the deposition process a portion of the C_3 vapor beam is condensed. Flash vaporization does then produce a C_3 burst. A possible interpretation of this result is that the C_3 molecules retain their identity in the chemisorbed layer. Two new experiments involving condensation from beams of isotopically labelled carbon vapor have been performed to shed new light on this phenomenon.

In the first of these, the new carbon atom source has been used to create a carbon vapor beam consisting almost entirely of isotopically enriched ($92\% \text{ }^{13}\text{C}$) carbon atoms. This beam is condensed on a polycrystalline graphite target of normal isotopic composition and the condensed layer is then flash desorbed. Regardless of the temperature of the condensing surface, the composition of the desorbed layer is always the same. Neither $^{13}\text{C}_3$ nor $^{12}\text{C}_3$ is observed in the flash desorbed layer. Furthermore, the amounts of C_2 observed seem to represent no enhancement over the very small amount of C_2 present in the incident vapor, nor are C_2 or C_3 observed in reflection of the atomic beam from the target. The conclusion is evident that combination of carbon atoms at the surface to form C_3 molecules does not occur, and combination of two atoms to form C_2 is at best a minor reaction.

The second experiment involves the use of an isotopically labelled beam of polyatomic carbon vapor. This beam is also condensed on a polycrystalline graphite target ($T_s < 800^\circ\text{K}$) of normal isotopic composition. In this experiment the isotopic distribution among flash desorbed C_3 molecules is monitored. A variation from the distribution in the incident beam will provide evidence of interaction of the condensed C_3 with atoms or molecules of the target surface. Such interaction has, in fact, been observed.

We have successively monitored the flash desorption of these carbon vapor species at mass 36 ($^{12}\text{C}_3$), mass 37 ($^{12}\text{C}_2^{13}\text{C}$), mass 38 ($^{12}\text{C}^{13}\text{C}_2$) and mass 39 ($^{13}\text{C}_3$) under reproducible conditions. The slow time constant of the standard ion detection system of the Nuclide mass spectrometer makes these observations qualitative in nature for masses 37, 38, and 39, and the sensitivity at mass 36 is limited by the large 36 peak which rises (although more slowly) from the target surface itself. Nevertheless, the results are quite clear cut in their general meaning. Roughly equivalent amounts of C_3 are desorbed at masses 37, 38, and 39. This is quite at variance with the isotopic ratios in the incident beam (Table IV). No flash desorption was detected at mass 36. The conclusion of these results is that a significant amount of isotopic exchange takes place between the target surface the the condensed adlayer. It seems likely that this exchange takes place during heating of the desorption temperature jump. This conclusion of isotope exchange is in keeping with the exchange techniques employed by Hoch and co-workers²⁶ to study condensation coefficients in the carbon vapor-graphite system.

VI. SUMMARY AND CONCLUSIONS

A set of experiments employing mass spectrometry and designed to elucidate various aspects of the kinetics and thermodynamics of graphite vaporization have been performed. A search for polymeric carbon vapor species in the free evaporation of polycrystalline graphites has produced evidence for several new species. At temperatures not exceeding 3000°K mass spectrometric signals corresponding to the ions C_{10}^+ , C_{11}^+ , C_{12}^+ , C_{14}^+ , and C_{15}^+ have been observed. These results are similar to some theoretical predictions. Three types of polycrystalline graphite have been used and both inductive and resistive heating have been employed. Although a rather wide scatter has been observed in the ion intensity vs. temperature data, this does not seem to be related to graphite type or heating method. Detection of these polymeric vapor species at the relatively low temperature of 3000°K together with the more intense signals at burnout of resistively heated samples encourages one to seek higher stable temperatures. Heating by laser beam or by continuous focussed electron beam should be excellent methods of producing the desired temperatures.

Careful examination of surface characteristics, reproducibility and stability of vapor composition and comparison with equilibrium studies lead one to the conclusion that surface porosity plays an important role in these studies. These pores and channels permit partial equilibration of the vapor, removing part of the distinction between free vaporization and equilibrium vaporization. Results from polycrystalline graphite should correspond to many engineering situations, but true free vaporization studies will require well-defined surfaces of pyrolytic graphite. On the other hand, designers wishing to employ polycrystalline graphite will need to recognize that the unequal rates of vaporization of binder and filler in commercial materials soon produces a porous material for which true free vaporization no longer exists.

Another facet of graphite behavior of possible interest to the designer is the large amount of outgassing produced upon heating most

commercial graphites. These gases consist primarily of hydrogen and carbon monoxide. For the experiments conducted in this program, a careful procedure of preheating is followed to minimize this phenomenon, but complete degassing is not accomplished. As we have noted previously,¹ impulse heating of previously unheated graphite specimens produces hydrogen as the most abundant desorbing species. This gas evolution may well be involved in the degradation of graphite specimens through particle emission.

The study of reflection/condensation behavior of carbon vapor at graphite surfaces has been extended by employing carbon vapor beams enriched in concentration of the ^{13}C isotope. This has permitted study of the reflected vapor beam without interference from normal surface vaporization at high temperatures. Measurement of isotope ratios in incident and reflected beams has provided a direct evaluation of the extent of gas-surface interaction during reflection. It was concluded that no observable isotopic exchange takes place during reflection of C_3 .

Atomic beams of isotopically enriched carbon have been used to demonstrate that atom combination on the surface to form C_2 or C_3 is not detectable. On the other hand, isotopically enriched C_3 which has condensed on a room temperature graphite surface of normal composition undergoes significant modification of isotopic composition upon desorption by temperature jump. It is clear that exchange with the surface has taken place. It will be most interesting to complete the study of flash desorption of condensed carbon vapors to obtain a measure of the forces acting between the condensate and the polycrystalline surface.

VII. REFERENCES

1. W.E. Welsh, Jr., "Proceedings of the Workshop on Graphite Ablation Held March 1971 at the Aerospace Corporation," Report No. TOR-017 (S2816-76)-11 (30 January 1972).
2. W.C. Steele, Technical Report AFML-TR-65-343, Part III (April 1968).
3. Konig, R.E., J. Chem. Phys., 22, 126 (1954).
4. Chupka, W.A. and M.G. Inghram, J. Chem. Phys., 21, 371 (1953).
5. Chupka, W.A. and M.G. Inghram, J. Chem. Phys., 21, 1313 (1953).
6. Chupka, W.A. and M.G. Inghram, J. Phys. Chem., 59, 100 (1955).
7. Drowart, J., R.P. Burns, G. DeMaria, and M.G. Inghram, J. Chem. Phys., 31, 1131 (1959).
8. Pitzer, K.S. and E. Clementi, J. Am. Chem. Soc., 81, 4477 (1959).
9. Strickler, S.J. and K.S. Pitzer in Molecular Orbitals in Chemistry, Physics, and Biology, (Pullman and Lowdin, eds.), Academic Press, New York, p. 281 (1964).
10. R.E. Duff and S.H. Bauer, J. Chem. Phys., 36, 1754 (1962).
11. Krieger, F.J., Memo RM-3326-PR, The Rand Corp. (September 1962).
12. T.A. Dolton, R.E. Maurer and H.E. Goldstein, AIAA 3rd Thermophysics Conference, Paper No. 68-754, Los Angeles, California (1968 June).
13. Kratsch, K.M., et al, Paper No. 68-1153, AIAA Entry Vehicle System and Technology Meeting, Williamsburg, Va. (3-5 December 1968).
14. Dorenburg, E. and H. Hintenberger, Z. Naturforsch., 14a, 756 (1959).
15. W.L. Baun and D.W. Fischer, J. Chem. Phys., 35, 1518 (1961).
16. Berkowitz, J. and W.A. Chupka, J. Chem. Phys., 40, 2735 (1964).
17. Wachi, F.M. and D.E. Gilmartin, Technical Report SAMSO-TR-69-124 (27 January 1969).
18. Zavitsanos, P.D., Final Report on Contract No. 16-7870 for Contract AT(929-1)-789 of Sandia Laboratories, (June 1970 - revised).
19. T.A. Milne, F.T. Greene, and S.L. Bennett, Technical Report AFML-TR-70-192 (February 1971).
20. Steele, W.C. and F.N. Bourgelas, Technical Report AFML-TR-71-77 (May 1971).

21. Chang, J.Y., Rev. Sci. Instr., 39, 756 (1968).
22. Hoffman, R., Tetrahedron, 22, 521 (1966).
23. Thorn, R.J. and G.H. Winslow, J. Chem. Phys., 26, 186 (1957).
24. Burns, R.P., A.J. Jason and M.G. Inghram, J. Chem. Phys., 40, 1161 (1964).
25. Zavitsanos, P.D., General Electric Report R66SD31, King of Prussia, Pa., (May 1966).
26. Hoch, M., T. Sskai, and D. Ramakrishman, Technical Report, AFML-TR-69-115, (April 1969).
27. Chupka, W.A., J. Berkowitz, D. J. Meschi and H.A. Tasman, in Advances in Mass Spectrometry, Vol. 2, p. 99, MacMillan, New York (1963).